LIQUEFACTION OF BLACK THUNDER COAL WITH COUNTERFLOW REACTOR TECHNOLOGY

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INTRODUCTION

There is currently a resurgence of interest in the use of carbon monoxide and water to promote the solubilization of low rank coals in liquefaction processes[1-3]. The mechanism for the water shift gas reaction (WGSR) is well documented[4,5] and proceeds via a formate ion intermediate at temperatures up to about 400°C. Coal solubilization is enhanced by CO/H_2O and by the solvent effect of the supercritical water. The WGSR is catalyzed by bases (alkali metal carbonates[6], hydroxides, acetates[7], aluminates[8]). Many inorganic salts which promote catalytic hydrogenation are rendered inactive in CO/H_2O[8,9], although there is positive evidence for the benefit of using pyrite for both the WGSR and as a hydrogenation catalyst[10].

The temperatures at which coal solubilization occurs are insufficient to promote extensive cracking or upgrading of the solubilized coal. Therefore, a two step process might achieve these two reactions sequentially. Alberta Research Council (ARC) has developed a two-stage process for the coprocessing of low rank coals and petroleum resids/bitumens[11]. This process was further advanced by utilizing the counterflow reactor (CFR) concept pioneered by Canadian Energy Developments (CED) and ARC. The technology is currently being applied to coal liquefaction. The two-stage process employs CO/H_2O at relatively mild temperature and pressure to solubilize the coal, followed by a more severe hydrocracking step. The counterflow reactor offers several advantages over co-current operations including: separation of the gas and light oil components, thus permitted a reduction in size of the reactors; concentration of the heavier components in the liquid phase such that their time spent in the reactors exceeds the nominal residence time; concentration of the active catalyst in the liquid phase; removal of the light components in the gas phase, resulting in less secondary cracking to gas. This paper describes the results of an autoclave study conducted to support a bench unit program on the direct liquefaction of coals.

EXPERIMENTAL

The procedure for the operation of the stirred autoclave (1 litre) has been described elsewhere[3]. Briefly coal (80g), solvent (120g), catalyst and water were charged into the autoclave. Carbon monoxide (400-800 psi) or hydrogen (1000 psi) was introduced, resulting in a typical operating pressure of 2500 ± 300 psi, depending on temperature and extent of the WGS reaction. The produced gas was discharged at ~150°C and collected. The autoclave flushed with a nitrogen purge (75L). Both gas samples were quantified by gas chromatography. Liquid products were transferred from the autoclave by addition of toluene at > 60°C (see later). Water, removed in the gas stream, was recovered by Dean-Stark extraction, at the same time toluene soluble oils (including asphaltenes) were extracted. The solid residue was further extracted with tetrahydrofuran (THF). The insoluble organic matter was determined following a proximate analysis. Asphaltenes were measured on an aliquot of the toluene soluble oils following removal of the toluene by a rotary evaporator. Attempts were made to distill the soluble oils. This procedure (D1160) proved ineffective, largely because of the solvent cut off point (about 450°C) which resulted in a poor reproducibility since there was little product in the 450-525°C range.

The solvent was obtained from Wilsonville, run number 263. Five barrels of V-1074 oils were received. These oils were sufficiently different in properties that a blend was prepared containing 20% from each barrel. The oils were extremely waxy and did not flow until 55-60°C. Black Thunder coal was provided by Thunder Basin Coal Company. It was partially dried prior to use to facilitate crushing and pulverization.

RESULTS and DISCUSSION
Solvent Stability

The solvent (V-1074 blend) had been produced from a hydrocracking process at Wilsonville and was partially hydrogenated (H/C mole ratio 1.16). Although listed as nominally boiling within the gas oil range, a crude simulated distillation found 14.2% of 525+ resid. A D1160 distillation of a similar material (Wilsonville Run 262) reported 95% of distillable by 501°C. Despite the apparent small amount of resid the V-1074 blend had 12.0% pentane insoluble asphaltenes.

Under standard 1st stage conditions (390°C/600 psi CO/30 minutes), Run 49, the solvent distillation range was virtually unchanged and gas yield was barely detectable (Table 1). At the highest temperature tested for 1st stage operation 410°C, gas yield was still below 1% and light oil distribution was stable. It took operation at 2nd stage conditions before a substantial change in solvent properties occurred, then decomposition to lighter oils and gas was evident. Throughout the range of conditions the asphaltene content remained almost constant suggesting that regressive reactions were not likely to present a problem in bench unit operations. Introduction of coal however might alter this observation. When 5% coal was introduced into the feed, asphaltenes increased from 12 to 19% under two-stage conditions.

Stoichiometry of the WGSR

The stoichiometry of the WGSR is complicated by the production CO and CO_2 from the coal, the presence of the K_2CO_3 catalyst and the reaction of hydrogen with the coal/solvent. In tests with this catalyst, the CO_2 produced exceeded the stoichiometric quantity from the CO consumption in the WGSR. Typically from 0.2-0.35 moles of excess CO_2 was found with a variety of catalysts or in the absence of catalyst (Table 2), which eliminated K_2CO_3 as the source. The water recovered was also between 0.2 and 0.30 moles less than predicted by the WGSR. In the absence of catalyst (Run 55) CO was actually produced, therefore it appeared that missing water could have reacted with CO from the coal to give CO_2. If this explanation is valid, then hydrogen consumption, defined as the difference between CO reacted and hydrogen produced, was greater than values previously reported[3]. This would not add to the economics of the process since this addition of hydrogen was derived from the coal and water, not from introduced CO.

Catalyst Activity

Literature reports agree that potassium carbonate is amongst the most effective WGSR catalysts. This work confirmed that K_2CO_3 out performed the other tested catalysts in terms of CO conversion, however this did not correlate with coal conversion (Table 2). When using FeS, Fe_2O_3/CS_2, K_2CO_3 or $NaAlO_2$, the coal conversions were all similar at 80-82% (repeat runs with K_2CO_3 gave a standard deviation of ±3%), yet the CO conversion ranged from 6-80%. Surprisingly the only runs which gave poorer coal conversion, were those using the molybdenum salts, ammonium molybdate (AM) and ammonium tetrathiomolybdate (ATM) or no catalyst. Apart from potassium carbonate, only the aluminate gave substantial CO conversion.

Petrographic examination of the residues gave some insight into the liquefaction process. With K_2CO_3 the vitroplast was almost completely solubilized, and what was left (2.7%) appeared little changed from the original coal. At the other extreme, i.e. without catalyst, there was no vitroplast present. Here the majority of the coal fragments were rounded cenospheres and vacuoles (72%), as is often seen with coal pyrolysis residues. Iron sulphide catalyst duplicated the results seen without catalyst (i.e. 66% cenospheres and vacuoles). In both cases only 9% CO conversion was recorded. $NaAlO_2$ was intermediate between these extremes for both CO conversion and residue appearance. A small portion of the coal remained as vitroplast (5%) while some vacuoles were formed (4%). The devolatilization process could ultimately lead to the formation of char. The presence of CO, when it underwent the WGSR, appeared to suppress this pathway to char. A high concentration of CO was required since vacuoles were also observed with syngas or CO/nitrogen atmospheres.

Liquefaction product yields were measured as asphaltenes, preasphaltenes and hydrocarbon gases (Table 3). The remaining products, including pentane soluble oils, carbon oxides and produced water, were grouped together as oils+, since their quantification was less reliable. Oils+ were, therefore, set numerically to the difference between the coal conversion and the sum of asphaltenes, preasphaltenes and hydrocarbon gases. This technique eliminated the need for corrections for mass balance, losses of light components during rotary evaporation of the toluene solubles, and changes in solvent composition during the run. Hydrocarbon gas yields at 390°C/30 minutes were consistent at 1.3-1.5g/100g MAF coal, irrespective of the catalyst employed. These values were independent of the coal conversion or the distribution of the distillable and non-distillable oils. Only a small portion of this gas could be attributed to solvent decomposition. The remainder was from thermal decomposition of the coal.

With the benchmark catalyst (K_2CO_3) the majority of the products were asphaltenes and preasphaltenes. The remaining catalysts (ATM, Fe_2O_3, AM) performed less favourably, yielding less oils+ or less total product. ATM did show increased activity in terms of the improved ratios of asphaltenes: preasphaltenes and oils+: preasphaltenes. This activity was confirmed when K_2CO_3 and ATM were combined which resulted in much lighter product slate (increased oils+, reduced asphaltenes and preasphaltenes) at similar coal conversion. This was one combination which was subsequently selected for the bench unit program.

Process Severity

Earlier work[3] had identified the minimum and preferred conditions for the solubilization of Black Thunder coal, but no work had been performed on the product yield distribution. Coal and CO conversion both increased with severity there was a noticeable progression from preasphaltenes --> asphaltenes --> oils+ with the K_2CO_3 catalyst (Table 3, Figure 1). This contrasted with the aluminate catalyst (410°C/30 min.)which had a sharp increase in asphaltenes (410°C/30 mins.) at the expense of oils+. Here solvent must have participated in regressive reactions to generate the additional asphaltenes. However the regressive reactions did not progress to preasphaltenes since little difference was seen between the K_2CO_3 and aluminate.

Simulated 2 stage tests were also performed. The test followed the standard procedure except that at the completion of the first stage the temperature was reduced to about 300°C, the CO gas was discharged and replaced with hydrogen. The temperature was raised to its new set point and the procedure continued. As anticipated there was a dramatic increase in process performance. Coal conversion rose to 91-95%. Preasphaltenes dropped to below 5% with FeS catalyst and almost zero with the molybdenum catalyst. Much of the asphaltene was also converted to oils+, especially with molybdenum where only a quarter of the products remained as asphaltenes or preasphaltenes. Gas production in the second stage was nominally 10-12g/100g coal, however much of this could be attributed to solvent breakdown.

Bench Unit Program

Much of the autoclave work was performed with potassium carbonate, as catalyst. Unfortunately this proved to be a poor practical choice because of the operational problems that arose due to its hydroscopic nature. In evitably the bench unit lines or valves plugged with solid potassium carbonate both when it was introduced as an aqueous solution or as a fine powder in the coal/solvent slurry. Ultimately it was replaced by the sodium aluminate, which showed no tendencies to deposit or plug the narrower parts of the Bench Unit.

Coal solubilization and CO conversion in the bench unit were below the level achieved in the autoclave at nominally similar process severity for single stage operation (Figure 2). It was not possible to directly compare CO conversion in the 2 operations for a variety of reasons e.g. gas residence time, CO:coal ratio and CO/H_2O mixing and contact were not the same. However, it can be seen that the trends observed in the autoclave were paralleled by the bench unit. Coal conversion approached 80% in the best runs when the temperature was raised to 410°C, but was consistantly about 10% less than the corresponding autoclave runs. This did not have a negative impact on the overall performance in the 2 stage operation as long as a shift catalyst was present. In the absence of a shift catalyst overall coal conversion was only 73% (Figure 3) for a 2 stage bench unit test at 440°C. Most of the product was asphaltenes, with less than 10% oils. When sodium aluminate was present overall conversion reached the maximum for coal conversion 92-94%. Under these conditions the product was primarily pentane soluble oils, with molybdate as usual better than iron based catalyst. Oil yield exceeded that found in the autoclave, but this technique again illustrated the trends ie., yield structure improved with process severity up to 440°C (2nd stage) and molybdate > iron catalysts. Therefore, the autocalve was a useful predictor of process performance.

The current bench unit is a once through operation. It is anticipated that further ocnversion of the asphaltenes to oils could be accomplished with recycle. Preliminary autoclave tests have confirmed that the bottoms product from the counterflow reactor (including ash, catalyst and IOM) can be upgraded to lighter products.

CONCLUSIONS

An effective shift catalyst is required to process Black Thunder coal. Once through counterflow reactor processing can yield greater than 60% pentane soluble oils. Autoclave tests can predict processing trends in the bench unit counterflow reactor.

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Table 1 : Solvent Stability Tests

	Solvent	1st stage	1st stage	2 stage
Conditions*	As received	410/600/30	390/600/30	440/1100/60
Catalyst		K2CO3	K2CO3/ATM**	FeS
CO conversion, %		57	66	H2
Gas yield,g/100g		0.8	0.1	2.5
Simulated Distillation				
IBP oC	297	153	176	138
IBP - 182oC	0.0	1.5	1.0	2.8
182 - 343oC	4.0	3.5	3.1	11.4
343+ oC	96.0	95.0	95.9	86.8

* temperature, oC; initial pressure, psi; time, minutes   ** Ammonium tetrathiomolybdate

Table 2 : Water Gas Shift Reaction

Run # *	Catalyst	CO	H2O	--->	CO2	H2	Coal conv
		Moles	Moles		Moles	Moles	%
28 in	K2CO3	1.23	1.88	--->	0	0	88
change		-0.96	-1.06		+1.19	+0.53	
31 in	K2CO3/N2	0	1.87	--->	0	0	50
change		0	-0.16		+0.20	0	
54 in	None	0	0.53	--->	0	1.27	55
change		+0.01	-0.03		+0.11	+0.27	
55 in	None	1.25	0.53	--->	0	0	62
change		+0.20	-0.20		+0.33	+0.02	
27 in	NaAlO2	1.25	1.88	--->	0	0	82
change		-0.56	-0.78		+0.89	+0.24	
26 in	FeS	1.26	1.88	--->	0	0	81
change		-0.09	-0.41		+0.49	+0.07	
36 in	K2CO3	0.85	1.45	--->	0	0	82
change		-0.59	-0.82		+0.88	+0.24	

* All runs at 390oC/600psi/30mins, except Run 36 at 370oC/400psi/30mins

Table 3 : Product Yield Distribution

Run #	Catalyst	Coal conv	CO conv	Asphalt	Preasp	Oils+	HC gas	Severity
		%	%	g/100g	g/100g	g/100g	g/100g	oC/psi/mins
37	K2CO3	82	80	45.5	24.4	10.7	1.4	390/600/30
51	K2CO3/ATM	80	79	37.4	18.6	22.5	1.4	*
53	ATM	73	6	39.1	20.4	12.0	1.3	*
58	Fe2O3/CS2	80	20	42.9	34.8	0.3	1.5	*
59	AM/CS2	75	20	46.2	26.6	0.3	1.5	*
25	None	78	9	n.d.			1.3	*
26	FeS	81	7	n.d.			1.4	*
27	NaAlO2	82	44		n.d.		1.4	*
35	K2CO3	88	83	55.0	10.8	19.3	2.9	410/800/30
36	K2CO3	61	70	32.1	22.7	5.5	1.2	370/400/30
57	NaAlO2	86	53	78.1	9.3	-5.0	3.5	410/600/30

Figure 1 : Product Yield Distribution

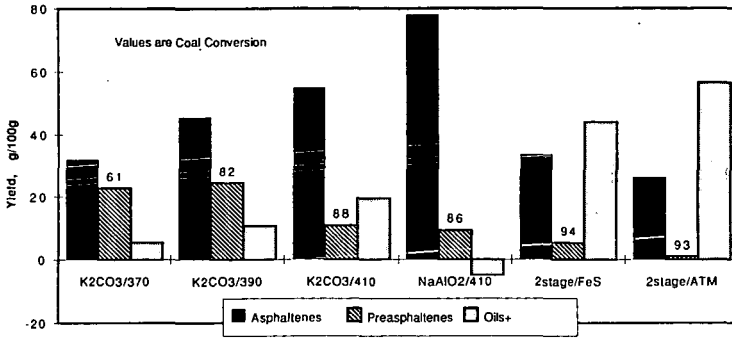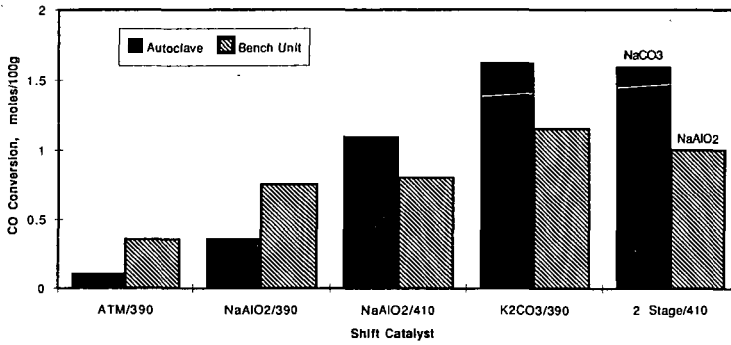Figure 1 : Product Yield Distribution

Figure 2 : Carbon Monoxide Utilization

Figure 3 : Performance of Bench Unit vs. Autoclave (2 Stage)